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Di-, Tetra-, and Polynuclear Copper(II) Complexes: Active Catalysts for Oxidation of Toluene and Benzene

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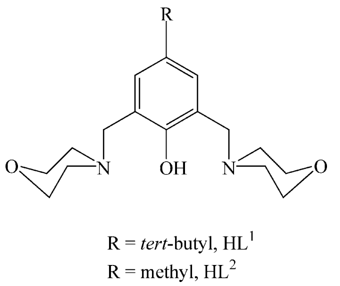
Three copper(II) complexes with a binucleating N_2O donor ligand, $[Cu_2(L^1)(\mu_2\text{-pz})(CH_3COO)_2]$ (**1**), $[Cu_4(\mathbf{L^1})_2(\mu_4\text{-O})(\mu_2\text{-}CH_3COO)_2(\mu_{1,1}\text{-}N_3)(N_3)]$ (**2**), and $[Cu_2(L^2)(\mu_{1,1}\text{-}N_3)(\mu_{1,3}\text{-}N_3)_2]_\infty$ (**3**) [pz = pyrazolato, HL^1 = 2,6-bis(morpholinomethyl)-4-*tert*-butylphenol and HL^2 = 2,6-bis(morpholinomethyl)-4-methylphenol] have been synthesized and characterized by elemental analysis, FTIR and UV/Vis spectroscopy, and X-ray crystallography. X-ray crystallographic studies revealed that a series of di-, tetra-, and polynuclear complexes have been formed by varying the bridging ligand, counteranion, and reaction conditions. These show effective catalytic properties for the hydrogen peroxide oxidation of toluene and benzene. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2008)

Introduction

Di-, tri-, tetra-, and polynuclear copper(II) complexes have been the subject of study by a large number of researchers, owing to the fact that copper, as an essential element present in biological systems, can carry out numerous catalytic reactions in living organisms.[1,2] These complexes also show interesting magnetic properties.[3] The desired nuclearity of coordination compounds in these networks can be specially tuned by subtle alterations in the structural and functional characteristics of organic ligands, the nature of the solvent, temperature and pH of the medium, the metal/ligand ratio, the template, and the counterions.[4] Although judicious and rational design of a reaction sequence may not lead to the formation of fully predictable frameworks,[5] one obvious point that should be taken into consideration is the proper choice of the spacer ligand, which plays a dominant role in the control and adjustment of the topology of the coordination framework.[3b]

The use of simple pyrazole,[6] azide,[7] or acetate[6b,8] as bridging or nonbridging ligands has been widely known. Among these, pyrazole-type heterocycles are considered to be versatile ligands that can interact with metal ions in several fashions: neutral monodentate, anionic monodentate, or *exo*/*endo* bidentate. A large number of pyrazole-bridged compounds have been prepared and characterized because of their interesting magnetic properties, catalytic activity, and bioactivity. Azide is another fascinating ligand, as it can perform as a mono-, bi-, tri-, or tetradentate ligand depending on the steric and electronic demands of the coligand.[9] It can mainly act as the end-on (EO) and end-to-end (EE) bridging mode.

We report here the syntheses and characterization of a series of copper(II) complexes, (e.g. di-, tetra-, and polynuclear complexes) with a dinucleating N_2O donor ligand (Scheme 1). X-ray crystallographic studies confirm the formation of di-, tetra-, and polynuclear copper(II) complexes depending on the nature of bridging ligand and counteranion. These show effective catalytic property for the hydrogen peroxide oxidation of toluene and benzene. We prefer toluene and benzene as the substrate for the catalytic reaction by using hydrogen peroxide as the oxidant. These substrates have been chosen because of their commercial importance as well as hazardous impact on the environment.[10] The controlled oxidation of toluene leads to a variety of products such as benzyl alcohol, benzaldehyde, and benzoic acid,[11] all of which are industrially very important. The oxidation of benzene leads to phenol, 1,4-dihydroxybenzene or higher oxidized products.[2i] Additionally, the oxidized products of toluene and benzene are environmentally less harmful than their corresponding parent



Scheme 1.

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compounds. Application of copper(II) complexes as the catalyst for the hydrogen peroxide oxidation of toluene to benzyl alcohol and benzaldehyde is rare. The use of copper complexes as catalysts for such reactions is scant.

Results and Discussion

Description of the Structures

Selected bond lengths and bond angles for complex **1**, **2** and **3** are given in Table 1. Complex **1** crystallizes in the monoclinic system, space group $P2_1/n$ from ethanol. A perspective view of $[Cu_2(L^1)(\mu_2\text{-pz})(CH_3COO)_2]$ (**1**) with the atom numbering scheme is shown in Figure 1. This is a discrete dinuclear complex. The asymmetric unit of complex **1** consists of two Cu^{2+} ions, one binucleating ligand, 2,6-bis(morpholinomethyl)-4-*tert*-butylphenolate (L^{1-}), one μ_2-pyrazolato, and two acetate ions. The five-coordinate copper(II) ions are linked by μ_2-phenoxido and μ_2-pyrazolato bridges that are well separated from each other. The intramolecular copper–copper distance is 3.292 Å. The Cu1 atom is coordinated by the μ_2-phenoxido O1 oxygen atom and the N1 nitrogen atom of the HL^1 ligand, the μ_2-pyrazolato N4 nitrogen atom, and the O6 and O7 oxygen atoms of same acetate moiety. In contrast, the Cu2 atom is connected by the O1 μ_2-phenoxido oxygen atom and the N2 nitrogen atom of the HL^1 ligand, the N3 μ_2-pyrazolato nitrogen atom, and the O4 and O5 oxygen atoms of the same acetate ions. The pentacoordinate copper atoms (Cu1 and Cu2) are in a distorted square pyramidal geometry, as is evident by the trigonal index, τ = 0.1417 and 0.2683 for Cu1 and Cu2, respectively. The value of τ is defined as the difference between the two largest donor–metal–donor angles divided by 60, a value that is 0 for the ideal square pyramid and 1 for the trigonal bipyramid.[12] The calculated values indicate a significant degree of distortion of the coordination geometry, particularly for the Cu2 atom. The four coordination sites of the quasisquare girdle are occupied by an oxygen atom and a nitrogen atom of the L^{1-} ligand, a nitrogen atom of the pyrazolato moiety, and an oxygen atom of the acetate ions. The Cu1 copper atom is displaced by 0.077 Å from the best plane formed by the N1, O1, O6, and N6 atoms. The displacement of Cu2 atom from the best plane formed by O1, N2, N3, and O4 is 0.134 Å. The axial position is occupied by O7 and O5 for Cu1 and Cu2, respectively. The axial Cu–O distances [Cu1–O7 2.457(2) and Cu2–O5 2.465(2) Å] are longer than the other Cu–O distances for both the copper atoms. The Cu–O and Cu–N distances vary from 1.940(2) to 2.465(2) Å and 1.930(2) to 2.047(2) Å, respectively. These agree well with the average Cu–O and Cu–N distances seen in previous reports.[13] The copper atoms are positioned in a distorted geometry where the angles subtended at the copper center vary from ca. 58.0(1) to 161.1(1)° (Table 1).

Table 1. Selected bond lengths (Å) and bond angles (°) of complexes **1**, **2** and **3**.

Complex **1**			
Cu1–O1	1.970(2)	Cu2–O1	1.940(2)
Cu1–O6	1.966(2)	Cu2–O4	1.950(2)
Cu1–O7	2.457(2)	Cu2–O5	2.465(2)
Cu1–N1	2.016(2)	Cu2–N2	2.047(2)
Cu1–N4	1.930(2)	Cu2–N3	1.937(2)
O1–Cu1–O6	161.1(1)	O1–Cu2–O4	157.9(1)
O1–Cu1–O7	103.2(1)	O1–Cu2–O5	100.5(1)
O1–Cu1–N1	95.1(1)	O1–Cu2–N2	90.1(1)
O1–Cu1–N4	89.2(1)	O1–Cu2–N3	90.5(1)
O6–Cu1–O7	58.2(1)	O4–Cu2–O5	58.0(1)
O6–Cu1–N1	93.5(1)	O4–Cu2–N2	98.7(1)
O6–Cu1–N4	90.8(1)	O4–Cu2–N3	94.9(1)
O7–Cu1–N1	105.5(1)	O5–Cu2–N2	100.4(1)
O7–Cu1–N4	99.8(1)	O5–Cu2–N3	117.0(1)
N1–Cu1–N4	152.6(1)	N2–Cu2–N3	141.8(1)
Complex **2**			
Cu1–O1	1.914(2)	Cu3–O3	1.947(2)
Cu1–O2	1.950(2)	Cu3–O5	2.350(2)
Cu1–O4	1.926(2)	Cu3–O6	1.948(2)
Cu1–N1	2.056(2)	Cu3–N3	2.076(2)
Cu2–O1	1.914(2)	Cu4–O1	1.944(2)
Cu2–O2	2.026(2)	Cu4–O3	1.956(2)
Cu2–O7	2.285(2)	Cu4–N4	2.049(2)
Cu2–N2	2.021(2)	Cu4–N5	1.937(2)
Cu2–N8	2.002(2)	Cu4–N8	2.525(2)
Cu3–O1	1.958(2)		
O1–Cu1–O2	81.15(8)	O1–Cu3–O6	92.92(7)
O1–Cu1–O4	93.13(8)	O1–Cu3–N3	168.10(8)
O1–Cu1–N1	168.50(8)	O3–Cu3–O5	93.41(8)
O2–Cu1–N1	89.65(8)	O3–Cu3–O6	168.39(8)
O2–Cu1–O4	165.93(7)	O3–Cu3–N3	89.00(7)
O4–Cu1–N1	97.34(8)	O5–Cu3–O6	94.37(8)
O1–Cu2–O2	79.22(8)	O5–Cu3–N3	97.33(7)
O1–Cu2–O7	94.54(7)	O6–Cu3–N3	98.54(7)
O1–Cu2–N2	168.36(8)	O1–Cu4–O3	79.31(7)
O1–Cu2–N8	89.04(8)	O1–Cu4–N4	170.86(8)
O2–Cu2–O7	91.43(7)	O1–Cu4–N5	97.53(9)
O2–Cu2–N2	93.20(8)	O1–Cu4–N8	74.59(8)
O2–Cu2–N8	161.76(8)	O3–Cu4–N4	93.77(7)
O7–Cu2–N2	94.48(7)	O3–Cu4–N5	162.51(11)
O7–Cu2–N8	103.47(8)	O3–Cu4–N8	90.32(8)
N2–Cu2–N8	96.01(9)	N4–Cu4–N5	90.84(9)
O1–Cu3–O3	79.20(7)	N4–Cu4–N8	99.69(8)
O1–Cu3–O5	84.94(8)	N5–Cu4–N8	105.53(10)
Complex **3**			
Cu1–O1	1.9766(11)	Cu2–O1	1.9676(12)
Cu1–N1	2.004(2)	Cu2–N1	1.989(2)
Cu1–N4	1.956(2)	Cu2–N7	1.952(2)
Cu1–N10	2.082(2)	Cu2–N11	2.0380(11)
Cu1–N6_b	2.334(2)	Cu2–N9_a	2.526(2)
O1–Cu1–N1	75.21(7)	O1–Cu2–N1	75.75(7)
O1–Cu1–N4	164.91(8)	O1–Cu2–N7	166.86(8)
O1–Cu1–N10	91.41(5)	O1–Cu2–N11	95.42(5)
O1–Cu1–N6_b	99.21(6)	O1–Cu2–N9_a	83.71(6)
N1–Cu1–N4	92.87(9)	N1–Cu2–N7	91.19(9)
N1–Cu1–N10	162.68(8)	N1–Cu2–N11	166.08(7)
N1–Cu1–N6_b	96.84(9)	N1–Cu2–N9_a	88.73(8)
N4–Cu1–N10	98.28(7)	N7–Cu2–N11	97.11(7)
N4–Cu1–N6_b	91.26(9)	N7–Cu2–N9_a	97.68(8)
N6_b–Cu1–N10	96.13(7)	N9_a–Cu2–N11	101.14(6)

a = 1 – *x*, –*y*, 1 – *z*. b = 1 – *x*, 1 – *y*, 1 – *z*.

Complex **2** crystallizes in the monoclinic system, space group $P2_1/c$ (No. 14) from water/ethanol. A perspective view of $[Cu_4(L^1)_2(\mu_4\text{-O})(\mu_2\text{-}CH_3COO)_2(\mu_{1,1}\text{-}N_3)(N_3)]$ (**2**) with the atom numbering scheme is shown in Figure 2. This

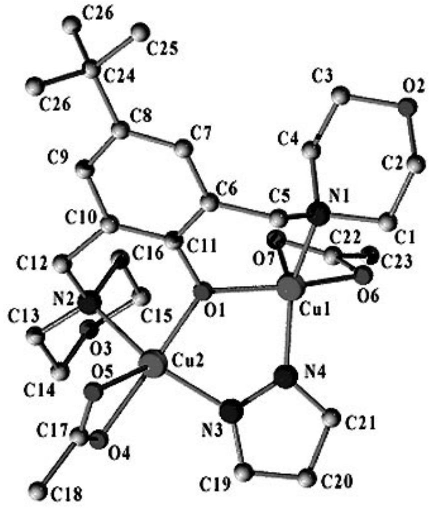

Figure 1. A perspective view of **1** with atom numbering scheme. Hydrogen atoms are omitted for clarity.

is a discrete tetranuclear complex. The asymmetric unit of complex **2** consists of four Cu^{2+}, one μ_4-oxido, two binucleating ligand, 2,6-bis(morpholinomethyl)-4-*tert*-butylphenolate (L^{1-}), two μ_2-acetate, one $\mu_{1,1}$-azide, and one azide ion. The Cu1 atom shows four coordination with the O2 μ_2-phenoxido oxygen atom and the N1 nitrogen atom of the binucleating ligand L^{1-}, the O1 μ_4-oxido oxygen atom, and the O4 μ_2-actetato oxygen atom. The copper atom is a distorted square-planar geometry with almost same Cu–O distances, whereas the Cu–N1 distance [2.056(2) Å] is slightly longer than the Cu–O distance (Table 2). The donor–metal–donor bond angles vary from 81.15(8) to 168.50(8)°. The Cu2 atom is coordinated by the O2 μ_2-phenoxido oxygen atom and the N2 nitrogen atom of the same binucleating ligand, the O1 μ_4-oxido oxygen atom, the O7 μ_2-actetato oxygen atom, and the N8 $\mu_{1,1}$-azide nitrogen atom. This copper atom is in a slightly distorted square pyramidal geometry as revealed by the trigonal index, $\tau = 0.11$. Cu2 is displaced by 0.214 Å from the best plane formed by O1, O2, N2, and N8. The axial position around the Cu2 atom is occupied by O7. The axial Cu–O distance [2.285(2) Å] is slightly longer than the basal distances. In contrast, the Cu3 atom shows five coordination and is connected by the O3 μ_2-phenoxido oxygen atom and the N3 nitrogen atom of the same binucleating ligand, the O1 μ_4-oxido oxygen atom, the O5 oxygen atom of a μ_2-actetato ion, which is bridged to Cu1 through O4, and the O6 oxygen atom of the μ_2-actetato ion, which is bridged to Cu2 through O7. This copper atom is in an almost perfectly square pyramidal environment as evident from the trigonal index, $\tau = 0.0048$. The O5 atom occupies the axial position. The Cu–O5 distance [2.350(2) Å] is slightly longer than other basal copper-donor distances. The fourth copper atom of the asymmetric unit, Cu4, is bonded through the O3 μ_2-phenoxido oxygen atom and the N4 nitrogen atom of the same binucleating ligand, the O1 μ_4-oxido oxygen atom, the N8 $\mu_{1,1}$-azide nitrogen atom, which is also connected to Cu2 and the N5 azide nitrogen atom. This copper atom is also in a distorted square pyramidal geometry as revealed from the trigonal index, $\tau = 0.1392$. The axial position is occupied by the N8 nitrogen atom. Here the axial Cu–N8 distance [2.525(2) Å] is slightly longer than the other distances. The bond angles around the Cu3 atom vary from 79.20(7) to 168.39(8)°. Cu4 is in a distorted square pyramidal geometry with bond angles ranging from 74.59(8) to 170.86(8)°. All the Cu–N and Cu–O distances are in accordance with previous reports.[13] The Cu–Cu distances of two Cu atoms bridged by the phenoxido oxygen atom are 2.976 (Cu1–Cu2, shortest distance) and 3.005 (Cu3–Cu4) Å. The longest Cu–Cu distance in this complex is 3.456 (Cu1–Cu4) Å.

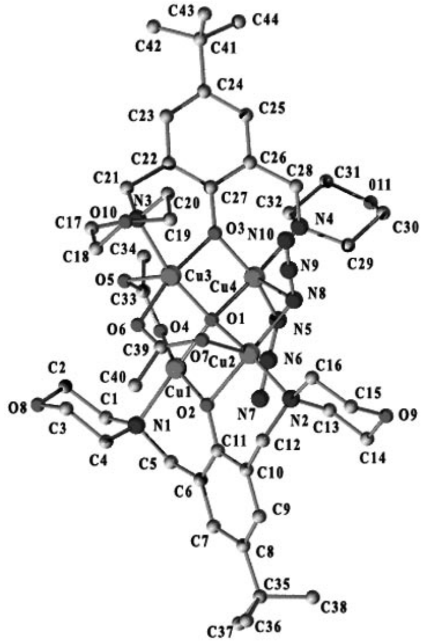

Figure 2. A perspective view of **2** with atom numbering scheme. Hydrogen atoms are omitted for clarity.

Complex **3** crystallizes in the triclinic, space group $P\bar{1}$ from water/methanol mixture solvent. The crystal structure of complex **3** consists of centrosymmetric dinuclear units of $[Cu_2(L^2)(\mu_{1,1}\text{-}N_3)(\mu_{1,3}\text{-}N_3)_2]$. Two copper(II) atoms are connected by a end-on azide bridge to define a centrosymmetric dimeric unit, each dimeric units is linked together to form a 1D chain (Figure 3). In complex **3**, the bridging azide anions exhibit two types of coordination modes: end-on fashion within the dimeric unit and end-to-end fashion between the neighboring dimeric units. One of the metal ions, Cu1 has a 4 + 1 distorted square-pyramidal environment whose basal plane (O1, N1, N4, and N10) comprises a μ_2-phenoxido oxygen atom (O1) and a nitrogen atom (N10) belonging to the binucleating ligand L^{2-} and two nitrogen atoms from the N1 end-on azide nitrogen and the N4 end-to-end azide nitrogen. The Cu1–O1 distance and Cu1–N distances are listed in Table 1. One N atom (N6) from the second azide of the end-to-end fashion occupies the axial position at a distance of 2.334(2) Å, with the Cu atom being

Table 2. Toluene oxidation[a] by complexes **1**, **2** and **3**.

Entry	Catalyst	$n(H_2O_2)$/n(catalyst)	Time (h)	Yield (%)			TON[b]
				Benz-aldehyde	Benzyl alcohol	Total	
1	**1**	200	6	7.1	18.2	24.3	6.1
2	**1**		48	8.6	28.5	35.1	8.8
3	**1**	400	6	12.2	27.6	39.8	10.0
4	**1**		48	19.6	29.4	47.3	11.9
5	**1**	800	6	14.0	18.2	32.2	8.1
6	**1**		48	16.1	21.5	37.6	9.5
7	**2**	200	6	13.6	28.5	42.1	10.6
8	**2**		48	14.0	31.3	45.3	11.4
9	**2**	400	6	14.1	29.7	43.8	11.0
10	**2**		48	22.2	32.1	54.3	13.7
11	**2**	800	6	21.9	29.9	51.8	13.0
12	**2**		48	25.6	34.6	60.2	15.2
13	**3**	200	6	8.2	16.0	24.2	6.10
14	**3**		48	11.3	16.0	27.3	6.9
15	**3**	400	6	8.60	20.9	29.5	7.3
16	**3**		48	11.1	29.9	40.0	10.1
17	**3**	800	6	7.6	15.2	22.8	5.7
18	**3**		48	8.1	16.1	24.2	6.1
19	$Cu(NO_3)_2$	200	48	1.1	2.2	3.3	
20	$Cu(NO_3)_2$	400	48	1.3	2.3	3.6	
21	$Cu(NO_3)_2$	800	48	1.3	2.5	3.8	

[a] Reaction time = 48 h, solvent = CH_3CN, room temperature, oxidant = hydrogen peroxide, n(HNO3)/n(catalyst) = 10. [b] TON: turnover number = mol of product/mol of catalyst.

displaced towards this apical site by 0.197 Å from the basal plane. The other copper atom Cu2 is connected by the O1 μ_2-phenoxido oxygen atom and the N11 nitrogen atom of the same binucleating ligand, the N1 $\mu_{1,1}$-azide nitrogen atom, and the N7 and N9 $\mu_{1,3}$-azide nitrogen atoms. The O1, N1, N7, and N11 atoms form the basal plane of the square pyramidal geometry, whereas N9 occupies the apical position. The Cu2–O1 and Cu2–N distances are given in Table 1. One N atom N9 from the second azide of end-to-end fashion occupies the axial position at a distance of 2.526(2) Å, with the Cu atom being displaced towards this apical site by 0.120 Å from the basal plane. Its crystal packing (Figure 4) can be rationalized in terms of centrosymmetric dimeric units held together by N4 and N6 of the azide group, which doubly bridge Cu1····Cu1 of two different dimeric units. These interactions generate a 1D chain along the crystallographic *b* axis. The Cu–Cu distance within the same asymmetric unit is 3.021 Å. The Cu1–Cu1 and Cu2–Cu2 distances of two adjacent asymmetric units are 5.125 and 5.183 Å.

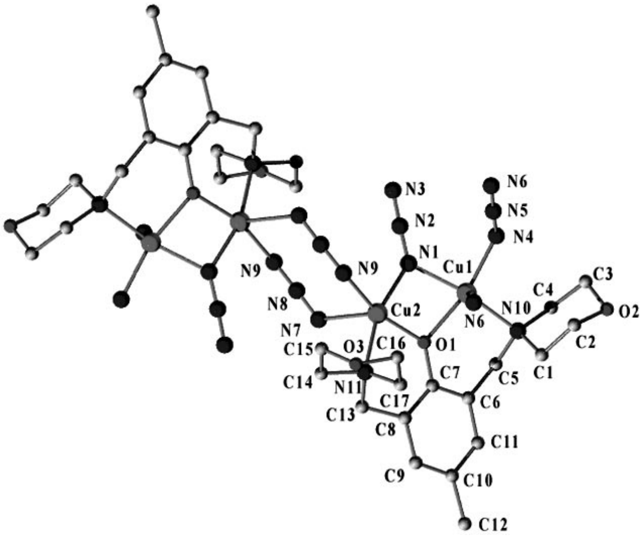

Figure 3. A perspective view of **3** with atom numbering scheme. Hydrogen atoms are omitted for clarity.

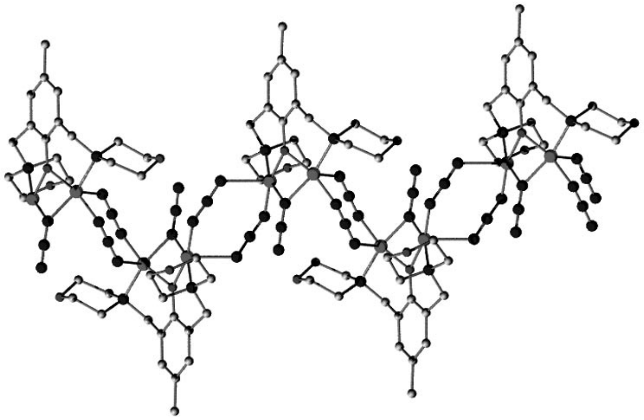

Figure 4. A perspective view of the 1D chain of complex **3** along the crystallographic *b* axis. Hydrogen atoms are omitted for clarity.

Oxidation of Toluene

Complexes **1**, **2** and **3** behave as active catalysts for the liquid biphasic (acetonitrile/water) oxidation of toluene by H_2O_2 in a slightly acidic medium at room temperature and atmospheric pressure. The corresponding products are benzyl alcohol and benzaldehyde in the case of toluene oxidation. Optimization has been achieved by varying the relative proportions of nitric acid, hydrogen peroxide, as well as time period of the reactions.

In earlier studies[1] with copper catalysts, it has been pointed out that the presence of nitric acid has a positive role. The catalyst activation is afforded by the increase in the unsaturation at the metal center with simultaneous increase in the oxidation properties. As a result, decomposition of peroxide is retarded and the peroxido intermediate is stabilized. We have shown that the addition of nitric acid is mandatory in the hydrogen peroxide oxidation of toluene in the presence of catalysts. The amount of oxidized products remains almost unchanged in the 10–50 range of $n(HNO_3)/n$(catalyst), whereas further increase in the ratio decreases the yield. When the oxidation of the substrate was carried out in absence of nitric acid, the reaction did not proceed. The highest conversion of the substrate was achieved when the ratio $n(HNO_3)/n$(catalyst) was 10 for all the catalysts. The geometry around the Cu center (except that of Cu1 in **2**, which is tetracoordinate) in all the catalysts is pentacoordinate having labile sites like Cu–N_3, Cu–μ_4-O, and Cu–acetate. These would require nitric acid so as to increase unsaturation at the metal site as a result of ligand protonation. Such observations evoked us to maintain a ratio of $n(HNO_3)/n$(catalyst) = 10 in the subsequent studies.

The results of toluene oxidation are shown in Table 2. It is clearly seen that the conversion of toluene is influenced by the relative amounts of hydrogen peroxide and the reaction period. The highest conversion of toluene among all the catalysts is obtained by complex **2** with 60.2% yield. The highest conversion of toluene is achieved with complexes **1** and **3** with 47.3 and 40.0% yields, respectively. High selectivity towards the formation of benzyl alcohol and benzaldehyde from the oxidation of toluene is exhibited by the complexes, as trace amounts of other byproducts were not detected by GC analyses of the final reaction mixture. Interestingly, formation of benzoic acid or *o*-, *m*-, or *p*-cresol was not detected during the analysis of the reaction mixture of toluene oxidation. In contrast, simple copper salts such as $Cu(NO_3)_2$ under the same reaction conditions exhibit a much lower activity towards oxidation of toluene with 3.3, 3.6, and 3.8% conversion under the same peroxide-to-catalyst molar ratio. As far as our knowledge goes, this is the first report of hydrogen peroxide oxidation of toluene to benzyl alcohol and benzaldehyde catalyzed by Cu^{II} complexes. The results of toluene oxidation are better or comparable with reported systems like copper-based binary metal oxides,[11c] Ru^{IV} complex,[14] $KMnO_4$,[15] and MCM-41 supported Cu–Mn catalyst.[11b]

Oxidation of Benzene

Complexes **1**, **2** and **3** were further tested for the oxidation reaction of benzene. The experimental results with these catalysts are shown in Table 3. The product detected in the biphasic (CH_3CN/H_2O) oxidation of benzene is exclusively phenol and other probable byproducts such as hydroquinone, catechol, resorcinol, etc. are not formed. The yield of phenol increases with time for all the reactions. We have performed these reactions at room temperature without altering other parameters where the conversion of benzene was found to be poor. The yield of phenol increases with an increase in the temperature. The catalytic reaction was carried out at 50 °C for 10 h. Under these conditions, complex **3** was found to be the most active catalyst for the oxidation of benzene to phenol with 9.1% yield, and complex **1** with 6.4% conversion of benzene is the least active catalyst in comparison to the other two. The conversion of benzene is 7.2% by using complex **2** as the catalyst. The reason for the use of nitric acid here is the same as that in the case of the oxidation of toluene. In view of much lower activity (Table 3) of a simple copper salt such as $Cu(NO_3)_2$ as a catalyst, it is evident that the presence of N,O donor ligands is quite relevant. Literature survey shows only one example where a monomeric Cu^{II} complex[2i] acts as a catalyst to oxidize benzene to phenol and *p*-benzoquinone. Our results are much improved with respect to the percentage yield and selectivity towards phenol compared to that of the Cu^{II} complex. These are also comparable to other systems like modified titanium silicate,[16] active vanadium species,[17] V-substituted heteropolyacid,[18] and vanadium oxide supported on mesoporous silica.[19]

Table 3. Benzene oxidation[a] by the complexes **1**, **2** and **3**.

Entry	Catalyst	Conversion[b] (%)	TON[c]
1	**1**	6.4	1.8
2	**2**	7.2	2.0
3	**3**	9.1	2.5
4	$Cu(NO_3)_2$	0.2	–

[a] Reaction time = 10 h, solvent = CH_3CN, temperature = 50 °C, oxidant = hydrogen peroxide, $n(HNO_3)/n$(catalyst) = 10. [b] Conversions were measured after 10 h of the reaction. [c] TON: turnover number = mol of product/mol of catalyst.

Mechanism

To identify the species that is responsible for the catalytic reactions, we recorded the UV/Vis spectra of the complexes with and without the addition of hydrogen peroxide and nitric acid. The UV/Vis spectra were recorded in the range 200–900 nm in acetonitrile, because this solvent was also used during the catalysis. The concentrations used were 1×10^{-4} M for all the complexes. As expected, all the complexes display similar band structure with or without the addition of hydrogen peroxide and nitric acid. The bands at 280 (ε = 7760 $M^{-1}cm^{-1}$), 288 (ε = 17690 $M^{-1}cm^{-1}$), and 291 (ε = 6930 $M^{-1}cm^{-1}$) nm are observed for complexes **1**, **2** and **3**, respectively. This may be attributed to π–π* transition within the ligand. The peaks at over 650 nm for all these complexes may be attributed to the d–d transitions. There is a broad shoulder in the region 335–425 nm for complex **1** (Figure 5). This is attributed to a phenolate Cu^{II} charge-transfer transition. The effect of the addition of hydrogen peroxide and nitric acid on the spectral characteristic of the complexes was examined. A sharp band at 395 nm with a shoulder around 420–440 nm appears upon addition of hydrogen peroxide, which may be attributed to the superposition of a peroxido Cu^{II} and a phenolate Cu^{II} charge-transfer transition. The broad band near 575 nm may also be a second less-intense peroxido Cu^{II} charge transfer transition. The UV/Vis spectra of complexes **2** and **3** in the presence of H_2O_2 were also recorded and similar results as in the case of complex **1** were obtained confirming the formation of (peroxido)copper(II) species. All the peaks/bands are in good agreement with the reported results of copper(II) complexes of closely relevant systems.[20] It is likely that a (peroxido)copper(II) species is formed during the catalytic process, and may act as the reactive species responsible for the transformation of the substrate. The electrospray mass spectra of complexes **1**, **2** and **3** were carried out in acetonitrile. The spectra of complexes **1**, **2** and **3** show peaks at 660.75, 1209.40, and 632.06, respectively. These peaks can be assigned to $[Cu_2(L^1)(pz)(CH_3COO)_2]$, $[Cu_4(L^1)_2(O)(CH_3COO)_2(N_3)_3(CH_3CN)]$,and$[Cu_2(L^2)(N_3)_3(CH_3CN)_2]$, respectively, as the theoretical isotopic distribution patterns are in excellent agreement with the experimental ones. Thus, in solution, complex **2** is a tetranuclear copper species, whereas complexes **1** and **3** are dinuclear species. This may account for the greater conversion of the substrate with complex **2** acting as the catalyst.

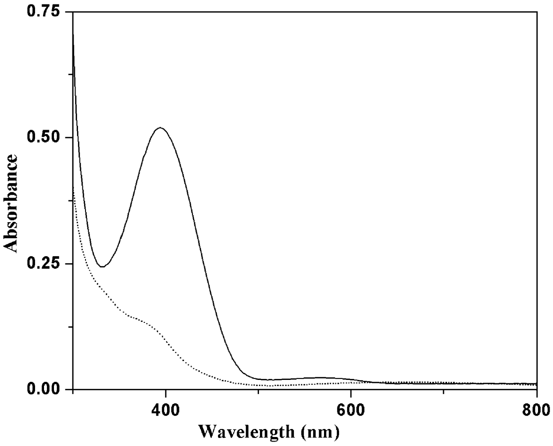

Figure 5. UV/Vis spectra of complex **1** with (solid line) and without (dashed line) the addition of hydrogen peroxide and nitric acid.

The most widely accepted mechanisms for the hydrogen peroxide oxidation are believed to occur by the formation of both carbon- and oxygen-centered radical species. As a consequence, when one carries out the reactions in the presence of a common carbon radical trap,[21] namely, $CBrCl_3$, TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl), or an oxygen-radical trap[21] (e.g. diphenylamine), a significant drop in the product yields is noted.

This, however, in no way discards the competitive nonradical pathways.[1] The formation of an organocopper intermediate may be envisaged resulting from an electrophilic attack that would involve an oxidized metal–peroxido, metal–oxido, or metal–superoxido moiety to activate the C–H bond of the substrate.[22] This can cleave the C–H bond heterolytically and has been amply demonstrated in earlier studies.[1] Concerted mechanisms of direct insertion of electrophilic oxygen atoms may also be operative.[2g]

Conclusions

We have synthesized and characterized a series of di-, tetra-, and polynuclear copper(II) complexes, $[Cu_2(L^1)(\mu_2\text{-}pz)(CH_3COO)_2]$ (**1**), $[Cu_4(L^1)_2(\mu_4\text{-}O)(\mu_2\text{-}CH_3COO)_2(\mu_{1,1}\text{-}N_3)(N_3)]$ (**2**), and $[Cu_2(L^2)(\mu_{1,1}\text{-}N_3)(\mu_{1,3}\text{-}N_3)_2]_\infty$ (**3**) [pz = pyrazolato, HL^1 = 2,6-bis(morpholinomethyl)-4-*tert*-butylphenol, and HL^2 = 2,6-bis(morpholinomethyl)-4-methylphenol] varying the bridging ligand, counteranion, and reaction conditions. These complexes are used as catalysts for the hydrogen peroxide oxidation of toluene under mild conditions. The results show that the catalysts convert the substrates to their oxidized products with better yield than the reported copper(II) complexes. The oxidation of benzene to phenol is also catalyzed by the complexes.

Experimental Section

Materials and Physical Methods: Copper(II) acetate monohydrate, copper(II) perchlorate hexahydrate, sodium azide, pyrazole, toluene, and benzene were purchased from Sigma Aldrich and used as received. All other reagents were of analytical reagent grade. Solvents used for spectroscopic studies were purified and dried by standard procedures before use.[23] FTIR spectra were obtained with a Nicolet MAGNA-IR 750 spectrometer with samples prepared as KBr pellets. Elemental analysis was carried out with a 2400 Series-II CHN analyzer, Perkin–Elmer, Norwalk, CT. Absorption spectra were carried out with a Shimadzu UV2100 UV/Vis recording spectrophotometer. The ESI-MS was recorded with a Qtof Micro YA263 mass spectrometer. Gas chromatography analysis was performed with an Agilent Technologies 6890N network GC system equipped with a fused silica capillary column (30 m × 0.32 mm) and a FID detector. All experiments were carried out in air and room temperature unless reported otherwise. The ligands HL^1, 2,6-bis(morpholinomethyl)-4-*tert*-butylphenol,[24] and HL^2, 2,6-bis(morpholinomethyl)-4-methylphenol,[20,25] were prepared according to published procedures.

$[Cu_2(L^1)(\mu_2\text{-}pz)(CH_3COO)_2]$ (1): Copper(II) acetate monohydrate (0.160 g, 0.8 mmol) was added slowly to a magnetically stirred of the HL^1 ligand (0.139 g, 0.4 mmol) in ethanol (10 mL), followed by the addition of triethylamine (0.081 g, 0.8 mmol). Pyrazole (0.026 g, 0.4 mmol) in ethanol (5 mL) was then added to the mixture dropwise. The mixture was stirred in air for 15 min and heated at reflux for 45 min. The mixture was cooled, filtered to remove any suspended material, and kept in air at room temperature. Green-colored single crystals of **1** suitable for X-ray crystallography were obtained on slow evaporation of the filtrate at ambient temperature within 2 d. Yield: 0.190 g (72%). $C_{27}H_{40}Cu_2N_4O_7$ (659.72): calcd. C 49.16, H, 6.11, N, 8.49; found C 49.06, H, 6.03, N, 8.34. FTIR (KBr phase): 1577 (vs), 1394 (s), 1383 (s), 1278 (w), 1176 (w), 1058 (m), 758 (m), 678 (w).

$[Cu_4(L^1)_2(\mu_4\text{-}O)(\mu_2\text{-}CH_3COO)_2(\mu_{1,1}\text{-}N_3)(N_3)]$ (2): Copper(II) acetate monohydrate (0.160 g, 0.8 mmol) was added slowly to a magnetically stirred solution of the HL^1 ligand (0.139 g, 0.4 mmol) in ethanol (10 mL) followed by the addition of triethylamine (0.040 g, 0.4 mmol) to the above solution. After that, sodium azide (0.026 g, 0.4 mmol) in water (5 mL) was added to the mixture drop by drop. The mixture was stirred in air for 15 min and then heated at reflux for 45 min. The mixture was cooled, filtered to remove any precipitate or undissolved substance, and kept in air at the ambient temperature. Black single crystals of **2** suitable for X-ray crystallography were obtained on slow evaporation of the filtrate at ambient temperature within 2 d. Yield: 0.327 g (70%). $C_{44}H_{68}Cu_4N_{10}O_{11}$ (1167.25): calcd. C 45.28, H, 5.87, N, 12.00; found C 45.16, H, 5.73, N, 11.94. FTIR (KBr phase): 3463 (br.), 2038 (vs), 1579 (m), 1485 (s), 1390 (m), 1315 (m), 1222 (w), 1112 (m), 671 (w).

$[Cu_2(L^2)(\mu_{1,1}\text{-}N_3)(\mu_{1,3}\text{-}N_3)_2]_\infty$ (3): To a solution of copper(II) perchlorate hexahydrate (0.296 g, 0.8 mmol) in methanol (10 mL) was added a solution of the HL^2 ligand (0.122 g, 0.4 mmol) in methanol

(5 mL) followed by the addition of triethylamine (0.4 mmol, 0.404 g). The mixture was stirred for 15 min. To this solution was dropwise added an aqueous solution (5 mL) of sodium azide (0.78 g, 1.2 mmol), and the mixture was stirred for 30 min and then heated at reflux for 1 h. The solution was cooled to room temperature, filtered to remove any suspended material, and the filtrate was kept in air at room temperature. The slow evaporation of the resultant solution led to dark-green crystals suitable for single-crystal X-ray diffraction. Yield: 0.145 g (65%). $C_{17}H_{25}Cu_2N_{11}O_3$ (558.54): calcd. C 36.56, H, 4.51, N, 27.59; found C 36.48, H, 4.43, N, 27.49. FTIR (KBr phase): 3445 (br.), 2100 (vs), 2062 (vs), 1614 (w), 1483 (s), 1284 (m), 1112 (s), 870 (w), 819 (w), 796 (w).

X-ray Data Collection and Structure Determination: Crystal data of complexes **1**, **2** and **3** are summarized in Table 4. The diffraction experiments were carried out with a Bruker SMART CCD area-detector diffractometer at 296 K for complexes **1** and **2** and at 150 K for **3**. No crystal decay was observed, so that no time decay correction was needed. The collected frames were processed with the software SAINT,[26] and an empirical absorption correction was applied (SADABS)[27] to the collected reflections. The calculations were performed by using the Personal Structure Determination Package[28] and the physical constants tabulated therein.[29] The structures were solved by direct methods (SHELXS)[30] and refined by full-matrix least-squares by using all reflections and minimizing the function $\Sigma w(F_o^2 - kF_c^2)^2$ (refinement on F^2). In compound **1**, atoms C25, C26, and C27 are disordered and split into three pairs having occupancy factors of 0.60 and 0.40. These atoms were refined with isotropic thermal parameters. All the other non-hydrogen atoms were refined with anisotropic thermal factors. The three hydrogen atoms bonded to C12 in **3** were refined with isotropic thermal parameters. All the other hydrogen atoms were placed in their ideal positions (C–H 0.97 Å), with the thermal parameter U 1.10 times that of the atom to which they are attached, and not refined. In the final Fourier map the maximum residuals were 2.18(41) e Å^{-3} at 0.10 Å from Cu1 in **1**, 1.94(39) e Å^{-3} at 0.23 Å from Cu1 in **2**, and 0.59(16) e Å^{-3} at 0.73 Å from N6 in **3**.

CCDC-664114 (for **1**), -664115 (for **2**), and -664116 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Oxidation of Toluene: Hydrogen peroxide (30% in H_2O, 2.5–10 mmol) was added to the metal complex (0.025 mmol) in acetonitrile (3 mL) in a two-neck round-bottomed flask fitted with a condenser. To this solution was added HNO_3 (0.25 mmol) followed by the addition of toluene (0.63 mmol). The reaction was initiated by stirring the mixture for 48 h at room temperature under atmospheric pressure. Aliquots were collected after regular time intervals and cyclopentanone (90 µL) was added as internal standard. The substrate and products from the reaction mixture were extracted with diethyl ether (10 mL) and analyzed by gas chromatography. The identification was achieved by comparison with known standards.

Oxidation of Benzene: For the oxidation of benzene, the reactions were performed in a magnetically stirred two-necked round-bot-

Table 4. Crystallographic information for **1**, **2** and **3**.

	$C_{27}H_{40}\,Cu_2\,N_4\,O_7$ (**1**)	$C_{44}H_{68}\,Cu_4\,N_{10}\,O_{11}$ (**2**)	$C_{34}H_{50}\,Cu_4\,N_{22}\,O_6$ (**3**)
Formula weight	659.72	1167.25	1117.08
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	10.498(1)	22.148(2)	10.278(1)
b (Å)	23.827(2)	10.545(1)	10.969(1)
c (Å)	12.114(1)	23.213(2)	11.716(1)
α (°)	90	90	111.56(1)
β (°)	95.67(1)	111.47(1)	110.70(1)
γ (°)	90	90	101.12(1)
V (Å^3)	3015.3(5)	5045.2(9)	1067.1(2)
Z	4	4	1
$D_{calcd.}$ (g cm^{-3})	1.453	1.537	1.738
μ (Mo-K_α) (mm^{-1})	1.461	1.733	2.043
Minimum and max. transmission factors	0.796–1.000	0.703–1.00	0.876–1.000
F (000)	1376	2424	572
T (K)	296	296	150
λ (Mo-K_α)	0.71073	0.71073	0.71073
Scan mode	ω	ω	ω
Frame width (°)	0.30	0.30	0.30
Time per frame (s)	35	20	20
No. of frames	1860	3360	2280
Detector-sample distance (cm)	6.00	6.00	6.00
Maximum and minimum θ (°)	27.0–3.0	27.0–3.0	27.0–3.0
Total data, unique data	29555, 7841	88091, 13393	12432, 5303
R_{int}	0.0550	0.0725	0.0175
Reciprocal space explored	full sphere	full sphere	full sphere
Final R_2 and R_{2w} indices[a] (F^2, all reflections)	0.077, 0.078	0.075, 0.072	0.043, 0.072
Conventional R_1 index [$I > 2\sigma(I)$]	0.041	0.040	0.027
Reflections with $I > 2\sigma(I)$	3750	7092	4170
No. of variables	358	622	310
Goodness-of-fit[b]	0.961	0.955	0.981

[a] $R_2 = [\Sigma(|F_o^2 - kF_c^2|)/\Sigma F_o^2]$, $R_{2w} = [\Sigma w(F_o^2 - kF_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [b] $[\Sigma w(F_o^2 - kF_c^2)^2/(N_o - N_v)]^{1/2}$, where $w = 4F_o^2/\sigma(F_o^2)^2$, $\sigma(F_o^2) = [\sigma^2(F_o^2) + (pF_o^2)^2]^{1/2}$, N_o is the number of observations and N_v the number of variables, and $p = 0.02$ for **1** and **2**, and 0.04 for **3**.

tomed flask fitted with a condenser and placed in a temperature-controlled oil bath for 10 h. Typically, the substrate (0.7 mmol) was dissolved in acetonitrile (5 mL) and to this solution was added the catalyst (0.025 mmol) and nitric acid (0.25 mmol). The mixture was then preheated to 50 °C. The reaction was started with the addition of hydrogen peroxide (30% in water, 5 mmol). Aliquots from the reaction mixtures were collected at regular intervals. After cooling, cyclopentanone (as the internal standard) and diethyl ether (5 mL) were added to extract the substrate. The substrate and product from the reaction mixture were analyzed by gas chromatography and identified by comparison with known standards.

Blank experiments for the oxidation of toluene and benzene were carried out without addition of any catalyst under the same experimental conditions, and no oxidized product in either case could be detected.

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